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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 59/305, 51/27		A1	(11) International Publication Number: WO 94/14745 (43) International Publication Date: 7 July 1994 (07.07.94)
(21) International Application Number: PCT/EP93/03693 (22) International Filing Date: 22 December 1993 (22.12.93)		(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 07/996,268 24 December 1992 (24.12.92) US		Published <i>With international search report.</i>	
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(54) Title: PREPARATION OF POLYOXYALKYLENE-ALPHA,OMEGA-DICARBOXYLIC ACIDS			
(57) Abstract			
<p>A process for the preparation of a polyoxyalkylene-alpha,omega-dicarboxylic acid by reacting the corresponding polyoxyalkylene glycol with a stable free radical nitroxide in the presence of a NO_x-generating compound and optionally, an oxidant and/or a solvent, at a temperature in the range of from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha,omega-dicarboxylic acid.</p>			

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PREPARATION OF POLYOXYALKYLENE-ALPHA, OMEGA-DICARBOXYLIC ACIDS

This invention relates to a process for the preparation of polyoxyalkylene-alpha,omega-dicarboxylic acids by the oxidation of the corresponding polyoxyalkylene glycols in the presence of a stable free radical nitroxide and a NO_x-generating compound.

5 Dicarboxylic acids are useful as chelating agents, detergent builders, and emulsifying agents. These acids, being composed of only the elements C, H and O, do not pose the environmental problems that other compounds containing heteroatoms such as N, S, and P pose. The alpha,omega-dicarboxylic acids can be prepared in
10 a two-step process by first reacting a glycol with ethylene oxide and an alkaline catalyst and thereafter converting the polyoxyalkylene glycol to a polyoxyalkylene-alpha,omega-dicarboxylic acid.

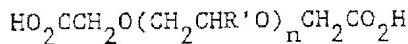
It is known from US patents Nos. 5,162,579; 5,166,422; 5,166,423; 5,179,218; 5,175,359; and 5,175,360 to use a stable free radical nitroxyl and a NO_x-generating compound (e.g., nitrous acid, nitric acid, nitrosodisulphonate, etc.) and/or a chlorine-containing oxidant (chlorine, hypochlorite) in the preparation of alkoxyalkanoic acids from the corresponding alkoxyalkanols. Although yield and selectivity in the disclosed processes are high, in
20 addition to the desired alkoxyalkanoic acids, also esters; formates; and (due to cleavage of the ether group) fatty acids have been found. Such processes would therefore appear not suitable for selective conversion of polyoxyalkylene glycols into the corresponding polyoxyalkylene-alpha,omega-dicarboxylic acids, as one would expect by-product formation comprising (cyclic) esters (due to the presence of both a carboxyl group and a hydroxyl group on the same molecule) and polyoxyalkylene-alpha-hydroxy-omega-carboxylic acids.
25

One would expect this problem to aggravate in case of only part of the polyoxyalkylene glycols is converted (for instance at starvation conditions, etc.).
30

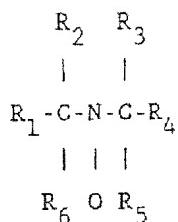
- 2 -

It has now surprisingly been found that polyoxyalkylene-alpha,omega-dicarboxylic acids can be produced in high yields and with high selectivities by using a stable free radical nitroxide and a NO_x-generating compound and optionally, an oxidant and/or a solvent.

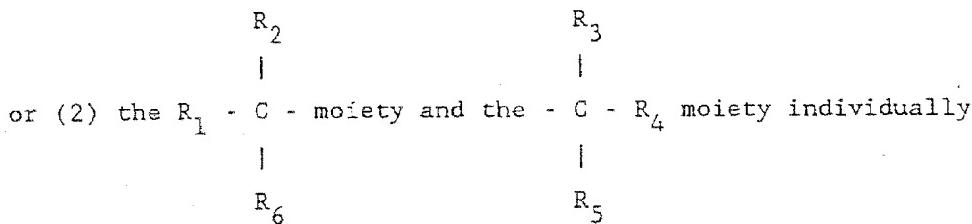
This invention relates to a process for the preparation of a polyoxyalkylene-alpha,omega-dicarboxylic acid of the formula:



wherein R' is hydrogen or methyl or mixtures thereof (on the individual molecule) and n is an integer of from 0 to 5,000 which comprises reacting the corresponding polyoxyalkylene glycol with a stable free radical nitroxide having the formula:



wherein (1) (a) each of R₁, R₂, R₃ and R₄ is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms, and (b) R₅ and R₆ (i) each is an alkyl group having 1 to 15 carbon atoms provided that R₁-R₆ are not all alkyl groups, or a substituted alkyl group having 1 to 15 carbon atoms wherein the substituent is hydrogen, cyano, -CONH₂, -OCOCH, OCOC₂H₅, carbonyl, alkenyl wherein the double bond is not conjugated with the nitroxide moiety, or -COOR wherein R of the -COOR group is alkyl or aryl, or (ii) together form part of a ring having at least two carbon atoms and up to two heteroatoms of O or N,

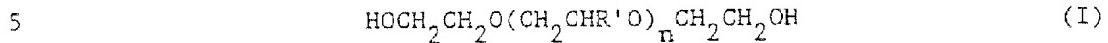


are aryl, in the presence of a NO_x-generating compound and optionally, an oxidant and/or a solvent, at a temperature in the range of

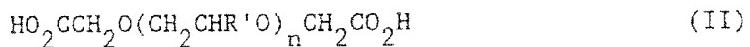
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from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha,omega-dicarboxylic acid.

The present process converts polyoxyalkylene glycols of the formula



wherein R' is hydrogen or alkyl, preferably methyl, or mixtures thereof (on the individual molecule) and n represents the average number of oxyalkylene groups and is an integer of from 0 to 5,000, preferably from 10 to 500, and more preferably 20 to 200, to the corresponding polyoxyalkylene- α,ω -dicarboxylic acids of the formula:



15 by contacting the polyoxyalkylene glycol with a stable free radical nitroxide in the presence of a NO_x -generating compound and optionally, an oxidant and/or a solvent, at a temperature in the range of from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha, ω -dicarboxylic acid.

The polyoxyalkylene glycol reactant suitably comprises one or more polyoxyalkylene glycols having a molecular weight in the range of from 100 to 250,000, preferably from 500 to 20,000, and more preferably from 1,000 to 10,000. The polyoxyalkylene glycols are typically prepared by the reaction of a glycol with an alkylene oxide in the presence of a suitable alkoxylation catalyst.

Glycols suitable for use in preparing the polyoxyalkylene glycol reactant in the present invention include ethylene glycol, diethylene glycol and triethylene glycol. In addition, glycols prepared by reacting ethylene oxide with water are also suitable for use in preparing the polyoxyalkylene glycol reactant in the present process. Specific glycols and glycol mixtures which are well known and are commercially available.

The process of the instant invention is particularly suited to alkoxylated glycols. In the case of propoxylated or alkoxylated glycols, it is necessary to further ethoxylate in order to obtain oxyalkylene-alpha,omega-dicarboxylic acids. The R' groups on an

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individual molecule can be hydrogen, methyl or mixtures thereof. For example, straight ethoxylated, straight propoxylated and mixed ethoxylated-propoxylated detergent range glycols are commercially available.

5 The term "stable free radical nitroxide" as used herein shall mean a free radical nitroxide that can be prepared by conventional chemical methods and will exist long enough to be used in a subsequent chemical reaction or examined in a static system by normal methods of spectroscopy. Generally, the stable free radical nitroxides of the present invention have a half life of at least one year. The term "stable free radical" shall also be understood to include the precursor to a stable free radical from which the stable free radical may be produced in situ.

10 The stable free radical nitroxides, as used in the present process, are precursors to catalysts, i.e., oxoammonium salts, active for the oxidation of glycols to the corresponding dicarboxylic acids. These catalysts are generated in situ by the oxidation of a stable free radical nitroxide to an oxoammonium salt with an oxygen-containing oxidant. The stable free radical nitroxide can be 15 obtained by the oxidation of secondary amines or hydroxylamines.

20 The stable free radical nitroxides which are suitable for use in the instant invention have the formula:



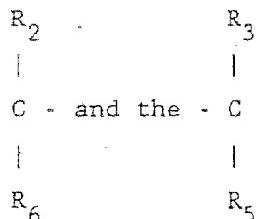
wherein each of R_1 , R_2 , R_3 and R_4 is an alkyl, aryl or heteroatom substituted alkyl groups and no hydrogen is bound to the remaining valences on the carbon atoms bound to the nitrogen. As used herein, 25 the term "alkyl" is meant to include cycloalkyl. The alkyl (or heteroatom substituted) groups R_1-R_4 may be the same or different, and preferably contain 1 to 15 carbon atoms. Preferable, R_1-R_4 are methyl, ethyl, or propyl groups. In addition to hydrogen, the

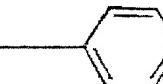
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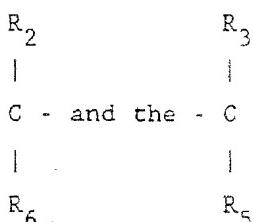
heteroatom substituents may include, halogen, oxygen, nitrogen and the like.

The remaining valences (R_5 and R_6) in formula III above may be satisfied by any atom or group except hydrogen which can bond covalently to carbon, although some groups may reduce the stabilising power of the nitroxide and are undesirable. When R_1 , R_2 , R_3 and R_4 are each alkyl groups, however, at least one of R_5 and R_6 must be an aryl group. Preferably, R_5 and R_6 are substituted alkyl groups having 1 to 15 carbon atoms wherein the substituent is selected from halogen, cyano, $-COOR$, wherein R is alkyl or aryl, $-CONH_2$, $-OCOC_2H_5$, carbonyl, or alkenyl where the double bond is not conjugated with the nitroxide moiety, or alkyl groups of 1 to 15 carbon atoms. R_5 and R_6 together may also form a ring of at least two carbon atoms and up to two heteroatoms, such as O or N.

Examples of suitable compounds having the structure above and in which R_5 and R_6 form part of the ring are piperidinyl-1-oxyls and pyrrolidin-1-oxyls.



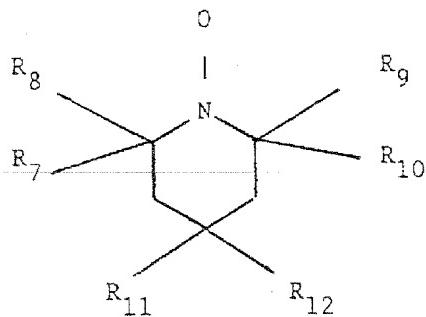
The $R_1 - C -$ and the $- C - R_4$ moieties in formula III above can individually be aryl, i.e., —  . Examples of suitable compounds



having the structure above in which the $R_1 - C -$ and the $- C - R_4$ moieties are individually aryl are diphenylamine, phenyl tertiary butylamine, 3-methyl-diphenylamines, 2-chlorophenylamine and the like. These compounds may be substituted with an substituents which do not interfere with the reaction.

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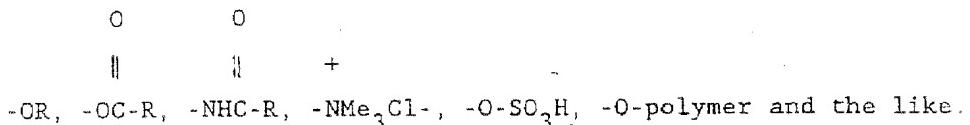
In a preferred embodiment, the stable free radical nitroxide has the formula:



wherein each of R₇, R₈, R₉ and R₁₀ is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms and no hydrogen

5 is bound to the remaining valences on the carbon atoms bound to the nitrogen, and each of R₁₁ and R₁₂ is alkyl, hydrogen, aryl or a substituted heteroatom. As used herein, the term "alkyl" is meant to include cycloalkyl. The alkyl (or heteroatom substituted) groups R₇-R₁₀ may be the same or different, and preferably contain 1 to 15 carbon atoms. Preferably, R₇-R₁₀ are methyl, ethyl, or propyl groups. In addition to hydrogen, the heteroatom substituents may include, halogen, oxygen, nitrogen and the like. Preferably, one of R₁₁ and R₁₂ is hydrogen, with the other one being a substituted heteroatom which does not interfere with the reaction. Suitable

10 15 substituted heteroatoms include



In a particularly preferred embodiment, the nitroxide is selected from the group consisting of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-pivoylamido-2,2,6,6-tetramethyl-piperidine-1-oxyl-4-sulphate, 4-alkoxy-2,2,6,6-tetramethyl-piperidine-1-oxyl, and mixtures thereof, with 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-pivoylamido-2,2,6,6-tetramethyl-piperidine-1-oxyl, and 4-alkoxy-2,2,6,6-tetramethyl-piperidine-1-oxyl being especially preferred.

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The NO_x -generating compound in the present process is typically selected from the group consisting of an alkali metal nitrosodisulphonate, nitric acid and mixtures thereof, with nitric acid being preferred. However, any compound which serves to generate NO_x during the course of the reaction and which does not interfere with the reaction would be suitable. While not wishing to be bound by any particular theory, it is believed that nitrogen oxides (NO_x) are generated in the reaction and are the active species in the reaction.

The alkali metal nitrosodisulphonate suitable for use as a NO_x -generating compound can be any alkali metal nitrosodisulphonate although potassium nitrosodisulphonate is preferred. As used herein, the term "alkali metal" is used as a descriptor of the elements Group IA of the Periodic Table of the Elements (Li, Na, K, Rb, Cs, Fr). The alkali metal nitrosodisulphonate is typically dissolved in water prior to being added to the reaction mixture although it can be added as a solid after all of the other reactants have been added.

As used herein, the term "nitric acid" refers to nitric acid, fuming nitric acid or nitrous acid generated by contacting a nitrate or nitrite salt such as, for example, an alkali metal salt, a tetraalkylammonium salt, an alkaline earth salt or a rare earth salt, with a strong acid such as, for example, a mineral acid. The nitric acid suitable for use as a NO_x -generating compound in the present invention typically has a concentration in the range of from 50 percent to 100 percent, preferably 70 percent. Generally, an amount of nitric acid in the range of from 5 mole percent to 1,000 mole percent, based on the moles of starting polyoxyalkylene glycol is utilised. The nitric acid is typically added to the reaction mixture after all of the other reactants have been added.

In a preferred embodiment, an oxidant is also added as a reactant. In general, when catalytic amounts of the NO_x -generating compound and nitroxide are used, the addition of an oxidant is preferred, whereas when stoichiometric amounts of the NO_x -generating compound and nitroxide are used, an oxidant may not be needed.

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One skilled in the art could readily determine by routine experimentation whether or not an oxidant would be useful in the reaction. The oxidants suitable for use in the instant invention are those compounds which are capable, in the presence of a NO_x-generating compound, of oxidising the stable free radical nitroxide to the oxoammonium salt. Suitable oxidants include oxygen-containing gases such as pure oxygen and oxygen in air. Whereas pure oxygen can is preferred to accomplish the desired conversion, the oxygen can also be diluted with an inert gas such as nitrogen, helium, argon, or other similar gas. While air can be used as the oxidant, the reaction rate is much slower. For purposes of increasing the reaction rate, higher O₂ pressures such as, for example, 7000 kPa (1000 psig) can be utilised. In a preferred embodiment, pure oxygen is used as the oxidant and it is bubbled into the reaction solution.

The reaction is preferably carried out in the presence of a solvent. When the molecular weight is such that the alkoxyalkanol reactant is a solid or a viscous liquid, a solvent in which the solid or highly viscous alkoxyalkanol reactant is soluble must be added. Suitable solvents are thus those in which the alkoxyalkanol reactant is soluble and those which do not interfere with the reaction. Suitable solvents include dichloromethane, triglyme, tertiary butyl alcohol, acetonitrile, carbon tetrachloride, monoglyme, diglyme, tertiary amyl alcohol and the like, and mixtures thereof. In a preferred embodiment, the solvent is selected from the group consisting of dichloromethane, acetonitrile, tertiary butyl alcohol and mixtures thereof. The weight ratio of solvent to alkoxyalkanol reactant is typically in the range of from 1:1 to 1:100, and preferably in the range of from 1:1 to 1:5.

The amounts and concentrations of the reactants utilised in the process of the instant invention can vary within wide ranges. The amount of stable free radical nitroxide is typically in the range of from 1 mole percent to 500 mole percent, preferably from 5 mole percent to 20 mole percent, based on the number of moles

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starting polyoxyalkylene glycol. Generally, the amount of NO_x generating compound used is in the range of from 5 mole percent to 1000 mole percent, based on the number of moles of polyoxyalkylene glycol.

5 The process of the present invention is typically conducted under mild conditions, with good results being obtained using a temperature in the range of from 0 °C to 100 °C, preferably 20 °C to 70 °C, and most preferably, 40 °C to 60 °C. Reaction pressures are not critical although higher pressures can result in increased
10 reaction rates. Pressures in the range of from atmospheric pressure up to about 7000 kPa (about 1000 psig) can be employed with good results.

15 The process of the instant invention can be carried out either batchwise or continuously, using a stirrer equipped reactor or other well known contacting technique to achieve adequate mixing. Preferred reaction conditions, e.g., temperature, pressure, flow rates, etc., vary somewhat depending on the specific nitroxide utilised and on the concentration of the nitroxide.

20 The process of the instant invention can be carried out in a variety of ways. For example, 0.0032 moles of the polyoxyalkylene glycol and 0.0064 moles of the nitroxide may be added to the reaction vessel, followed by the addition of 0.011 moles of 70 percent nitric acid. Following the reaction, the product may be separated from the reaction mixture using conventional procedures such as, for example, an extraction procedure or a precipitation procedure. The particular procedure utilised depends on whether the reaction product is a solid or liquid at room temperature. If the product is solid at room temperature, precipitation is typically used. If, however, the product is a liquid at room temperature, an extraction procedure is generally used. The reaction product can be purified by a number of conventional means such as high temperature water washing or catalytic hydrogenation.

25 Depending upon process conditions and the nitroxide used, the yields of polyoxyalkylene-alpha,omega-dicarboxylic acid obtained by this invention can be greater than 98% of starting material being

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converted. The products produced by the instant process can be used in a variety of detergent applications. For example, corrosion inhibitors, detergent builders or emulsifying agents.

5 The ranges and limitations provided in the instant specification and claims are those which are believed to particularly point out and distinctly claim the present invention. It is, however, understood that other ranges and limitations which perform substantially the same function in the same or substantially the same manner to obtain the same or substantially the same result are 10 intended to be within the scope of the instant invention as defined by the instant specification and claims.

The process of this invention will be further described by the following embodiments which are provided for illustration and are not to be construed as limiting the invention.

15 Illustrative Embodiments

Example 1

20 10.9 Grams of poly(ethylene glycol) having a molecular weight of 3400, 1.0 grams of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 50 millilitres of acetonitrile and 1 gram of 70 percent nitric acid were charged to a 100 millilitre round bottomed flask. O₂ was bubbled through this mixture at ambient pressure. The reaction temperature was held at 35 °C over a 6-hour period. The results are presented in Table I.

Example 2

25 100 Grams of poly(ethylene glycol) having a molecular weight of 3400, 5 grams of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 200 millilitres of methylene chloride and 5 grams of 70 percent nitric acid were charged to a 500 millilitre round bottomed flask. Air was bubbled through this mixture at ambient pressure. The 30 reaction was held at reflux over a 8-hour period. The results are presented in Table I.

Example 3

35 10.9 Grams of poly(ethylene glycol) having a molecular weight of 3400, 1 gram of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 50 millilitres of acetonitrile and 1 gram of 70 percent nitric acid

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were charged to a 100 millilitre round bottomed flask. The reaction mixture was held open to the atmosphere. The reaction temperature was held at 35 °C over a 6-hour period. The results are presented in Table I.

5 Example 4

10.9 Grams of poly(ethylene glycol) having a molecular weight of 3400, 0.2 grams of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 50 millilitres of methylene chloride and 0.2 grams of 70 percent nitric acid were charged to a 100 millilitre round bottomed flask. 10 O_2 was bubbled through this mixture at ambient pressure. The reaction temperature was held at 35 °C over a 5-hour period. The results are presented in Table I.

Comparative Example A

15 Comparative Example A was carried out in a manner similar to Example 1 except that no nitroxide was used. The results are presented in Table I.

Comparative Example B

20 Comparative Example B was carried out in a manner similar to Example 4 except that no nitric acid was used. The results are presented in Table I.

Comparative Example C

Comparative Example C was carried out in a manner similar to Example 4 except that no nitroxide was used. The results are presented in Table I.

25 As can be seen in Table I, nitroxide and nitric acid are necessary for the oxidation of the terminal diol to proceed.

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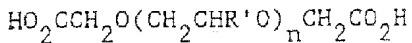
Table I

Oxidation Of Polyoxyalkylene Glycols to
Polyoxyalkylene-Alpha-Omega Dicarboxylic Acids

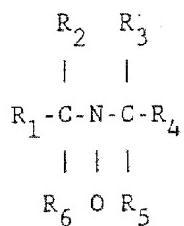
	% Conversion	% Selectivity to Dicarboxylic Acids
Example 1	>99	>99
Example 2	>99	>99
Example 3	>99	>99
Example 4	56	90
Comparative Example A	0	0
Comparative Example B	0	0
Comparative Example C	0	0

C L A I M S

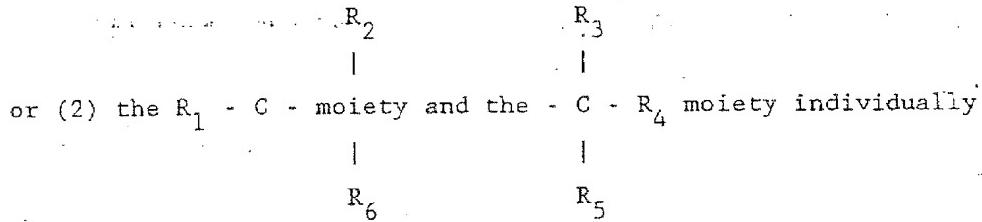
1. A process for the preparation of a polyoxyalkylene-alpha,omega-dicarboxylic acid of the formula



wherein R' is hydrogen or methyl or mixtures thereof (on the individual molecule) and n is an integer of from 0 to 5,000, which comprises reacting the corresponding polyoxyalkylene glycol with a stable free radical nitroxide having the formula:



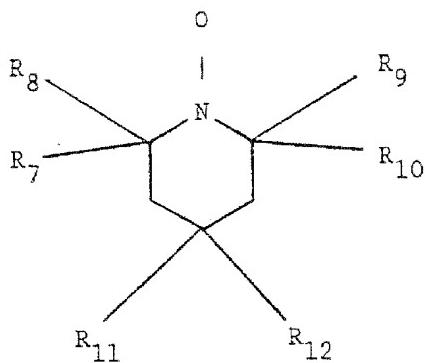
wherein (1) (a) each of R₁, R₂, R₃ and R₄ is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms, and
 10 (b) R₅ and R₆ (i) each is an alkyl group having 1 to 15 carbon atoms provided that R₁-R₆ are not all alkyl groups, or a substituted alkyl group having 1 to 15 carbon atoms wherein the substituent is hydrogen, cyano, -CONH₂, -OCOCH, OCOC₂H₅, carbonyl, alkenyl wherein the double bond is not conjugated with the nitroxide
 15 moiety, or -COOR wherein R of the -COOR group is alkyl or aryl, or (ii) together form part of a ring having at least two carbon atoms and up to two heteroatoms of O or N,



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are aryl, in the presence of a NO_x -generating compound and an oxidant at a temperature in the range of from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha,omega-dicarboxylic acid.

- 5 2. The process of claim 1 wherein the stable free radical nitroxide has the formula:



wherein each of R_7 , R_8 , R_9 and R_{10} is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms and each of R_{11} and R_{12} is alkyl, hydrogen, aryl or a substituted heteroatom.

- 10 3. The process of claim 3 wherein the stable free radical nitroxide is selected from the group consisting of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-pivoyleamido-2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-alkoxy-2,2,6,6-tetramethyl-piperidine-1-oxyl and mixtures thereof.
- 15 4. The process of any one of claims 1-3 wherein said NO_x -generating compound is nitric acid.

5. The process of any one of claims 1-4 wherein the amount of NO_x -generating compound is in the range of from 5 mole percent to 1,000 mole percent, based on the number of moles polyoxyalkylene glycol.
- 20 6. The process of any one of claims 1-5 wherein said polyoxyalkylene glycol is contacted with said stable free radical nitroxide, followed by the addition thereto of said NO_x -generating compound and said oxidant.

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7. The process of any one of claims 1-6 wherein the amount of stable free radical nitroxide is in the range of from 1 mole percent to 500 mole percent, based on the number of moles of polyoxyalkylene glycol.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 93/03693

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07C59/305 C07C51/27

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 162 579 (FRIED) 10 November 1992 cited in the application see column 2, line 28 - line 51 see claims 1-15 ----	1,4,5
Y	US,A,3 888 877 (LEHN) 10 June 1975 see column 25; example 1 see column 29; example 13A see column 42; example 47A -----	1,4,5

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
5 April 1994	14.04.94

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 93/03693

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